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CALCULATION OF THE DIPOLE MOMENTS OF TRI-SUBSTITUTED BENZENES

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ABSTRACT. A general method is given for the calculation of dipole moments of 1, 2, 4 tri-substituted benzenes taking into account the induced effects, similar to the treatment of Smallwood and Herzfeld for the di-substituted compounds. The calculated values are given for five compounds for which the observed values are available and a comparison is made between the calculated and observed values.

INTRODUCTION

The dipole moments of poly-substituted benzenes calculated by the simple vectorial addition of the individual group moments reveal wide divergences between the calculated and the observed values in a majority of cases. Such divergences may arise from several causes, such as, the electrostatic attractions and repulsions, the induced effects or the occurrence of mesomerism etc. In the case of the di-substituted benzenes the induced effects are computed by Smallwood and Herzfeld (1930) adopting the plane hexagonal model for the benzene ring in the substituted compounds. This has provided a valuable correction. LeFevre and LeFevre (1936, 1937) applied the method for diphenyl, coumarin, and xanthone ring systems. Each atom or group is regarded as a sphere of uniform polarisability and the induced moments are calculated by assuming that this sphere is subjected to a field which is that produced at the centre of the sphere by the primary dipole. Smyth and McAlpine (1933) calculated the induction in each bond and obtained the bond polarisabilities in terms of the bond refractions. Groves and Sugden (1937) pointed out that when the atom or group is very near the primary dipole, allowance must be made for the variation of the field over the volume of the atom and this is done by means of the method of graphical integration suggested by Frank (1935).

THEORY

In this paper the method of calculation of Smallwood and Herzfeld is extended to the case of 1,2,4 tri-substituted benzenes. The resultant moment of a tri-substituted benzene compound is regarded as comprising of (1) the vector sum of the moments of primary dipoles, (2) the mutual induction of the three primary dipoles on one another and (3) the moments induced in the $-CH$ and $-C-C$ bonds of the hydrocarbon residue by the primary dipoles.

Figure 1 represents the case of a 1, 2, 4 substituted compound. The appropriate angles and distances may be understood from figure 2. The

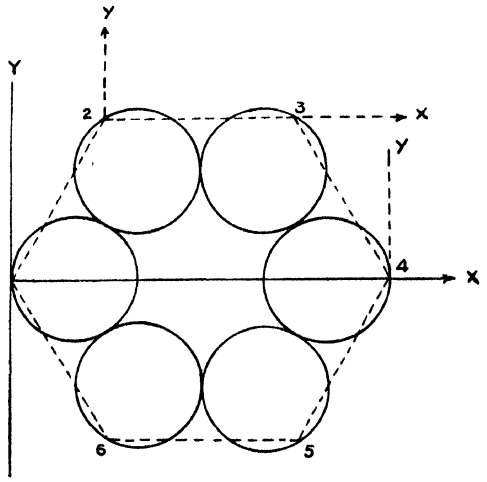

FIG. 1

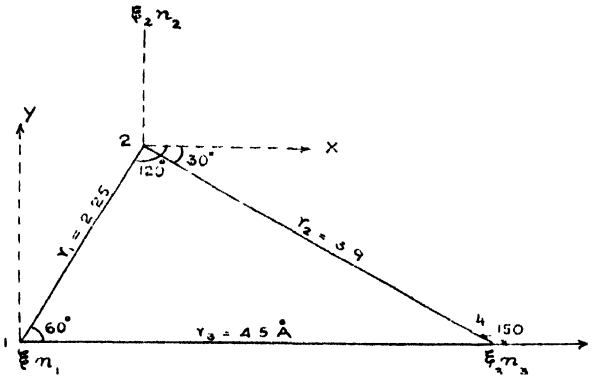

FIG. 2

notation used is the same as that of Smallwood and Herzfeld. ξ_1, ξ_2, ξ_3 represent the x-components and η_1, η_2, η_3 the y-components of m_{01}, m_{02} and m_{03} respectively. Using their equations and referring to figure 2, the interaction of the three dipoles on one another gives the following relations.

$$
\left.
\begin{aligned}
&\xi_1^1 + (a_1/4)\xi_2^1 - 2a_3\xi_3^1 - (3\sqrt{3}/4)a_1\eta_2^1 = \xi_1 \\
&(b_1/4)\xi_1^1 + \xi_2^1 - (5/4)b_2\xi_3^1 - (3\sqrt{3}/4)b_1\eta_1^1 + (3\sqrt{3}/4)b_2\eta_3^1 = \xi_2 \\
&2c_3\xi_1^1 + (5/4)c_2\xi_2^1 - \xi_3^1 - (3\sqrt{3}/4)c_2\eta_2^1 = -\xi_3 \\
&-(3\sqrt{3}/4)a_1\xi_2^1 + \eta_1^1 - (5/4)a_1\eta_2^1 + a_3\eta_2^1 = \eta_1 \\
&(3\sqrt{3}/4)b_1\xi_1^1 - (3\sqrt{3}/4)b_2\xi_3^1 + (5/4)b_1\eta_1^1 - \eta_2^1 - (b_2/4)\eta_3^1 = -\eta_2 \\
&(3\sqrt{3}/4)c_2\xi_2^1 + c_3\eta_1^1 + (c_2/4)\eta_2^1 + \eta_3^1 = \eta_3
\end{aligned}
\right\} \quad (1)
$$

where

$\alpha_1/r_1^3 = a_1$, $\alpha_1/r_2^3 = a_2$, $\alpha_1/r_3^3 = a_3$.
$\alpha_2/r_1^3 = b_1$, $\alpha_2/r_2^3 = b_2$, $\alpha_2/r_3^3 = b_3$.
$\alpha_3/r_1^3 = c_1$, $\alpha_3/r_2^3 = c_2$, $\alpha_3/r_3^3 = c_3$.

α_1, α_2 and α_3 represent the polarisabilities of the three substituent groups.

The fields of the induced moments are also considered in the above equations since we have written $\xi^1 = \xi + \xi_i$ and $\eta^1 = \eta + \eta_i$. Thus as a result of dipolar induction each ξ is modified to a certain ξ^1 and each η is modified to a certain η^1. In order to obtain the numerical values for ξ^1 and η^1 the six equations (1) are solved by the method of post-multiplication giving the values for the six variables.

The induced moments in the remaining $-CH$ groups at 3, 5 and 6 are calculated along similar lines. The values of the angles (v) and distances (r) are given in Table I. The data given in Table I are from Smallwood and Herzfeld, page 1921.

TABLE I.

Group		(3)	(5)	(6)
I	r	3.0	3.0	2.25 Å
	v	30°	−30°	−60°
II	r	2.25	1.5	3.0
	v	0°	−60°	−90°
III	r	2.25	2.25	3.0
	v	120°	−120°	−150°

The total induced effect in the $-CH$ groups at 3,5 and 6 is given as

$$\left.\begin{aligned}\Sigma\,\xi_i = 0.01320\xi_1^1 + 0.07456\eta_1^1 + 0.1021\xi^1{}_2 - 0.009324\eta^1{}_2 \\ - 0.01939\xi^1{}_3 + 0.01432\eta^1{}_3 \\ \Sigma\,\eta_i = -0.07456\xi_1^1 + 0.06624\eta_1^1 - 0.009324\xi^1{}_2 - 0.02641\eta^1{}_2 \\ + 0.01432\xi^1{}_3 + 0.1406\eta^1{}_3\end{aligned}\right\} \quad \ldots \quad (2)$$

In evaluating the induced moments in the C−C bonds, the various angles and distances used are given in Table II. These values are derived using simple trigonometrical relations from the data in Table I, assuming plane hexagonal model for the benzene ring.

TABLE II.

Group		(1)	(2)	(3)	(4)	(5)	(6)
I	r	1.3	2.6	3.438	3.138	2.6	1.3 Å
	v	30°	30°	11°	−11°	−30°	−30°
II	r	1.3	2.6	3.438	3.438	2.6	1.3
	v	30°	−30°	−49°6′	−70°54′	−90°	−90°
III	r	1.3	2.6	3.438	3.438	2.6	1.3
	v	−150°	−150°	−169°	169°	150°	150°

The total induced moment in this case is obtained as

$$\left.\begin{aligned}\Sigma\,\xi_i^1 &= 1.3520\,\xi_1^1 + 0.2150\,\xi_2^1 - 0.7098\,\eta_2^1 + 1.3520\xi_3^1\\ \Sigma\eta_i &= -\,0.2952\eta_1^1 - 0.7098\xi_2^1 + 0.9399\eta_2^1 - 0.2952\eta_3^1\end{aligned}\right\} \quad \ldots\ (3)$$

Combining eqns. (2) and (3) the result is

$$\left.\begin{aligned}\Sigma(\xi_i^1 + \zeta_i) &= 1.3652\xi_1^1 + 0.07456\eta_1^1 + 0.3171\xi_2^1 - 0.7191\eta_2^1\\ &\quad + 1.3326\xi_3^1 + 0.01432\eta_3^1\\ \Sigma(\eta_i + \eta_i^1) &= -0.07456\xi_1^1 - 0.2290\eta_1^1 - 0.7191\xi_2^1 + 0.9135\eta_2^1\\ &\quad + 0.01432\xi_3^1 - 0.1546\eta_3^1\end{aligned}\right\} \quad \ldots\ (4)$$

Finally the resultant moment M of the molecule is given as

$$M = \sqrt{M_x^2 + M_y^2} \qquad \ldots\ (5)$$

where

$$M_x = 2.3652\xi_1^1 + 1.07456\eta_1^1 + 1.3171\xi_2^1 + 0.2809\eta_2^1 + 2.3326\xi_3^1 + 1.01432\eta_3^1$$
$$M_y = 0.9254\xi_1^1 + 0.7710\eta_1^1 + 0.2809\xi_2^1 + 1.9135\eta_2^1 + 1.0143\xi_3^1 + 0.8454\eta_3^1.$$

RESULTS

The final results for the five compounds considered, together with the observed values of Hassel and Naeshagen (1931) and Lutgert (1932) are tabulated in Table III.

TABLE III

Compound	M_{vect}	M_{eq} (5)	M'	M_{obs}	m_c value assumed
1, 2, 4 trichlorobenzene	1.64	1.24	1.40	1.25	$m_c = 1.64$
2, 4 dinitrochlorobenzene	3.26	3.11	3.19	$3.0 \pm .1$ 3.29	$m_{c1} = 1.64$ $m_{c2} = 3.75$
2, 4 dinitrobromobenzene	3.26	3.72	3.51	$3.1 \pm .1$	$m_{c1} = 1.56$ $m_{c2} = 3.75$
2, 4 dinitroiodobenzene	3.31	4.92	4.29	$3.4 \pm .1$	$m_{c1} = 1.25$ $m_{c2} = 3.75$
2, 5 dichloronitrobenzene	3.75	3.31	3.48	3.15	$m_{c1} = 1.64$ $m_{c2} = 3.75$

The values under the column (M_{vect}) are obtained by the simple vectorial addition. The second column gives the values calculated using Eqn (5). It is very difficult to judge which value of m_c (the moment of the mono-substituted compound) is to be used in the calculation since, for the same mono-substituted compound various values have been reported in the literature. For uniformity the values of Hojendahl (1929) are assumed throughout. In the case of the iodo-compound, since his value is not available the value of Walden and Werner (1929) is used. It is unfortunate that there are no values available for the tri-substituted compounds by the same authors whose values are assumed for m_c. Thus, in view of the fact that the experimental values for the mono-and the tri-substituted compounds are determined by

different authors and since the values are liable to vary, the calculated and observed values may not be expected to agree closely. From Table III we note that a closer approximation to the observed values is obtained by using Eqn (5) than in the case of M_{vect} for three of the compounds studied (1, 2, 4 trichlorobenzene, 2, 4 dinitrochlorobenzene and 2, 5 dichloronitrobenzene). The polarisabilities of the groups increase as we go from chloro to bromo- to the iodo-compound and hence the induced effects also increase in the same direction. As we see from the table, the deviation between the calculated and the observed values also increases in the same direction.

In the above calculations, a correction for the dielectric constant of the internuclear space is also considered. LeFevre and LeFevre (1937) pointed out that the calculated induced moment must be reduced by the factor $(\varepsilon+2)/3\varepsilon$ (ε being the dielectric constant of the internuclear space) in order to obtain the actual induced moment. The value of ε is obtained as 2.40 from measurements of the variation of the dielectric constant of benzene with pressure. Groves and Sugden also remarked that little error will be introduced by assuming $\varepsilon=2.40$ in the case of aromatic compounds. The reduction factor turns out to be 4.4/7.2. The values obtained when this correction is applied are given under the column headed M' in Table III. The difference between M_{eq} (5) and M_{vect} gives the induced moment. This difference multiplied by the factor 4.4/7.2 gives the actual induced moment. This is added algebraically to M_{vect} to give the value under M'. By this process, the agreement with the observed value is improved for all the compounds studied except 1, 2, 4 trichlorobenzene where the induced contribution to the moment is considerably large.

The assumptions in the above method and other errors will have to be clearly stated. (1) The assumption that the dipoles are situated at the circumference of the carbon atoms to which the groups are attached, is an approximation. Smyth (1934) remarks that a consideration of the location of the centre of gravity of the charges assignable to the carbon halogen portion of the molecule in the halogenated compounds indicates the most probable location of the principal dipole to be approximately 7/8 of the distance from the carbon nucleus to the halogen nucleus. But the first assumption is adopted, as otherwise the calculations become extremely complicated. (2) The distances between the various groups enter in the third power in the equations used for computing the induced moment, Hence a small error in the distance may cause a relatively large error in the final value of the moment. (3) The method has not taken into account the variation of the field of the dipole over the volume of the atom or group in which the moment is induced, since the distances under consideration are all greater than 1 A.U. The equation, assuming proportionality between the induced moment and the field of the primary dipole ($m_i=\alpha E$), breaks down at close distances. (4) Rotation round the bonds may also affect the

of the particle ($2\pi r$) and the wavelength of light (λ). There are marked changes in the intensity distribution of scattered light even for small changes in either the radius of the particle, the refractive index of the particle or the wave length of light used. It is possible to obtain the theoretical curves for the angular distribution of the intensity of scattered light by particles of different size parameters α and of different refractive indices. A comparison of the experimental curves of the intensity distribution of scattered light with the theoretical curves gives an estimate of the size of the particles.

DISSYMMETRY OF SCATTERED LIGHT

The second method is based on the dissymmetry of scattered light in the forward and the backward directions. Debye (1946) has worked out the theory of this method for particles of small refractive index. The details of theory and the experimental technique are described by Oster (1948), Mark (1947), and Zimm, Stein and Doty (1945). The Debye theory is not directly applicable to particles of large refractive indices. A study of the Mie scattering functions for particles of different sizes and of different refractive indices indicates, however, a possibility of the application of the dissymmetry method to particles of large refactive indices upto a certain limit of the sizes of the particles. A theoretical evaluation of the dissymmetry of the intensity of scattered light for particles of refractive index as large as 2, indicates that the dissymmetry, i.e., the ratio of the intensities of scattered light about two symmetrical angles in the forward and the backward directions, goes on systemtically increasing with the radius of the particles upto a certain size parameter $\alpha(=2\pi r/\lambda$, r being the radius of the particles and λ being the wavelength of light used). Beyond this value of α, the dissymmetry ratio begins to fluctuate with increasing α and has a number of maxima and minima. It is, therefore, possible to compare the experimental and theoretical dissymmetry values, and to estimate the size of the particles, provided the value of α lies below the given limit.

SCOPE OF THE PRESENT INVESTIGATION

The present investigation was, therefore, undertaken to determine the sizes of colloidal particles by using the above two mutually independent methods based on the scattering of light and also to see how far the two methods are in agreement with each other. Two sols, viz. Fe_2O_3 and As_2S_3 of refractive indices 2.40 and 2.67 respectively, are selected for this purpose. Their relative refractive indices with respect to water are 1.8 and 2 approximately. These sols were prepared according to the methods described by Trivedi and Pattani (1952). Double-distilled water and pyrex vessels were used in all stages of the experiment.

METHOD BASED ON THE ANGULAR DISTRIBUTION OF SCATTERED LIGHT

By using the data from Lowan's Tables (1949), two sets of theoretical curves for the intensity distribution of scattered light by particles of refractive indices 1.8 and 2, and of different size parameters α ($\alpha < 2$) were obtained. The values of the scattering functions for refractive index 2 are directly available from the tables, but for refractive index 1.8, interpolation was used for obtaining these values. It was found that as the values of the scattering functions increase uniformly with α upto a value 6 for all refractive indices of the particles, this method of interpolation would be applicable in the present case and would not involve much error. Beyond $\alpha=6$, the scattering functions fluctuate rapidly with a large number of maxima and minima and hence interpolation would not be possible. While plotting these curves, the values of the intensity functions were normalized by taking the intensity of scattered light in a transverse direction (i.e. 90°) as unity for a given curve. These curves are shown by dotted lines in figures 2 and 3 for Fe_2O_3 and As_2S_3 respectively. The α value for each curve is indicated in the diagrams. In these curves, the direction of incidence (i.e. forward direction) is taken as zero degree.

Experimental.

In order to investigate the angular distribution of scattered light by the particles of the sol, a photo-cell was mounted on the telescope arm of a spectrometer. A monochromatic beam of light from a strong source was made to be incident through the collimator tube on a circular trough containing the colloidal solution. As the beam converged a little on entering the trough, the incident beam was focused by a lens on a small aperture in the collimating tube and a slightly divergent beam of light from this aperture entered the trough in such a way that the convergence due to the trough made the beam parallel on entering the trough. The experimental arrangement is shown in figure 1. Two suitable standardised

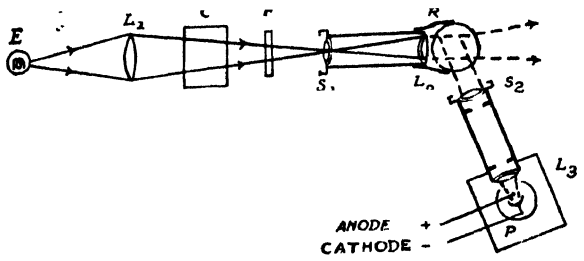

FIG. 1. Experimental arrangement
E—Source of light, L_1, L_2,—collimators, *C*—water cell, *F*—light filter, S_1, S_2– slits, *R*—rubber guard ring, L_3—converging lens, *P*—photocell

Kodak filters, having narrow transmisssion bands in the region of 5000 A.U. and 6550 A.U., were selected for getting monochromatic beam of light.

spherical size. Still however, the layout of the experimental curves does indicate a similarity with one or two adjoining theoretical curves. The values of the radii of the particles of the two sols are given in Table I.

TABLE I

Radius of particles from angular scattering of light

Sol	Refractives index	Wavelength in A.U.	α	Radius in μ	Mean radius in μ
Fe_2O_3	1.8	6550	0.5	0.039	0.037
		5000	0.6	0,035	
As_2S_3	2	6550	0.65	0 043	0.042
		5000	0.70	0.041	

METHOD BASED ON DISSYMMETRY OF SCATTERED LIGHT

The theoretical values of the dissymmetry of scattered light for particles of different sizes and of relative refractive indices 1.8 and 2 were obtained by taking the ratio of the intensity functions I_{45} and I_{135} of scattered light at angles of 45° and 135° respectively (incident direction being taken as zero degree). These dissymmetry ratios are obtained from the data available in Lowan's tables of light scattering functions. These values of dissymmetry are shown graphically in figures 4 and 5 for two sols of refractive index 1.8 and 2 respectively. The dissymmetry ratio I_{45}/I_{135} is expressed by the symbol Z.

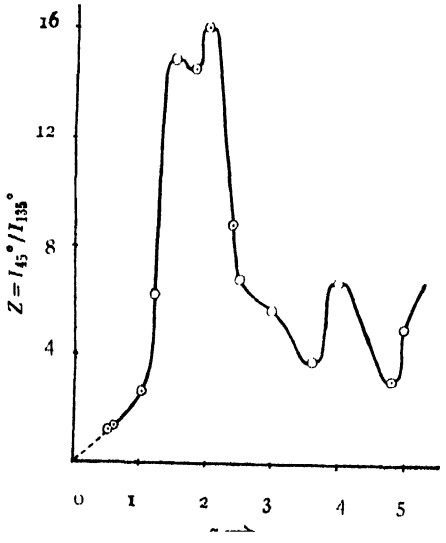

FIG. 4. Theoretical variation of dissymmetry with α for Fe_2O_3 refractive index = 1.8)

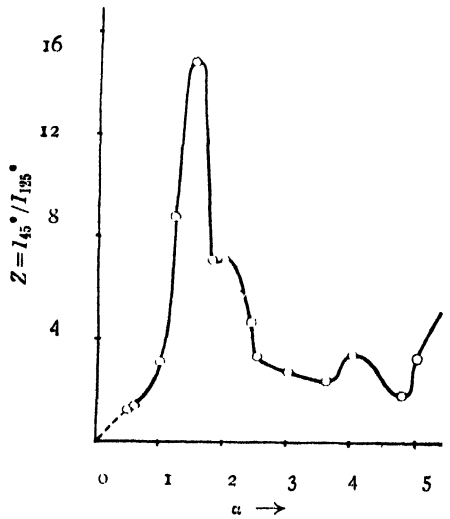

FIG. 5 Theoretical variation of dissymmetry with α for As_2S_3 (refrative index = 2)

The curves show that the dissymmetry function increases systematically with α upto a certain value, beyond which it begins to oscillate and gives rise to a number of maxima and minima. It can be seen that so long as the dissymmetry ratio lies below a value 3 for paricles of refractive index 1.8, there is only one value of α for a given value of the dissymmetry ratio. Similarly so long as the dissymmetry ratio lies below a value 1.82 for particles of refractive index 2, there is only one value of α corresponding to a given value of the dissymmetry ratio.

If, therefore, the experimental dissymmetry values lie below 3 for Fe_2O_3 sol of relative refractive index 1.8, and below 1.82 for As_2S_3 sol of relative refractive index 2, it would be possible to estimate the size parameter α and hence the radius of the particles from an experimental determination of the dissymmetry ratios for the two sols. By using two wavelengths of light for the dissymmetry measurements, it becomes possible to obtain two independent α values for the same sol by this method. A mean value of the radius of the particles can then be obtained from these α values.

Experimental.

The experimental procedure consists in measuring the intesity I_{45} and I_{135} of scattered light of a given wavelength along 45° and 135° angles

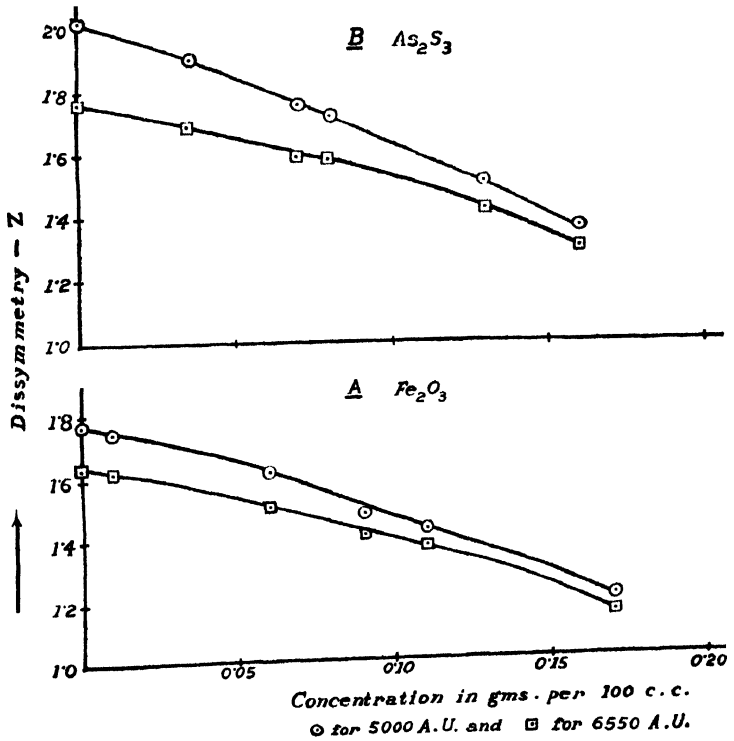

FIG. 6. Graph showing the variations of dissymmetry with concentration.
B. For As_2S_3 sol. *A*. For Fe_2O_3 sol.

respectively. The same photoelectric photometer was used for this purpose. As the dissymmetry function is found to be dependent on the concentration to some extent, it is necessary to derive the value of the dissymmetry ratio at infinite dilutions for each wavelength of light used. The dissymmetry ratio I_{45}/I_{135} was, therefore, determined for five different concentrations of a given sol for each wavelength of light used. The dissymmetry ratio at infinite dilution, which is also known as the intrinsic dissymmetry 'Z', is determined by extrapolation of the curve of dissymmetry ratio versus concentration in each case. These curves are given in figures 6*A* and 6*B* for Fe_2O_3 and As_2S_3 respectively. By using the values of the intrinsic dissymmetry, the values of α corresponding to each wavelength of light used was obtained from the theoretical dissymmetry ratio curves for the sol concerned. The radius of the particles r, can be calculated from the relation $\alpha = \frac{2\pi r}{\lambda'}$, where λ' is the wavelength of light in water. The results of these measurement are summarised in Table II. Again, in order to compare the values of the radii determined by the two optical methods, both the sets of results are summarised in Table III.

TABLE II

Radius of particles from dissymmetry

Sol	Relative refractive index	λ in A.U.	Experimental dissymmetry	α	Radius in μ	Mean radius in μ
Fe_2O_3	1.8	6550	1.62	0.66	0.052	0.048
		5000	1.77	0.73	0.044	
As_2S_3	2.0	6550	1.78	0.72	0.056	0.052
		5000	20.2	0.80	0.048	

TABLE III

Comparison of radii of particles from two optical methods

Sol	Radius of particles in μ		
	Angular scattering method	Dissymmetry method	Mean
Fe_2O_3	0.037	0.048	0.042
As_2S_3	0.042	0.052	0.047

The above results indicate that the values of the radii determined by the dissymmetry method are slightly higher than those determined by the angular scattering method. It is, however, likely that the dissymmetry method should be more reliable than the angular scattering method, because it involves intensity measurements at two specific angles and they can be done more accurately and quickly than a number of angular intensity measurements. If, therefore, intrinsic dissymmetry is determined accurately for any sol, it would give a reliable measure of the size of the particles of a sol if α is smaller than a given value for each sol. It will be necessary to construct a theoretical dissymmetry curve in each case.

As it is likely that the refractive index of the particles in the sol may not be exactly the same as that of the bulk material, dissymmetry values for different refractive indices varying from 1.33 to 2.0 were obtained from Lowan's Tables. It was, however, found that all the dissymetry curves do not differ appreciably from each other upto $\alpha = 1.5$. The maximum difference in the values of dissymmetry for a given α, does not exceed by more than 15 per cent for variation of the values of refractive index from 1.33 to 2.0. Thus any small variation of the relative refractive index of the sol particles from the bulk material would not appeciably change the value of the radius of the particles determined by the present dissymmetry method.

CONCLUSIONS

The present investigation shows that it is possible to estimate the size of the particles by two independent methods based on Mie (1908) theory. The dissymmetry method due to Debye (1946) can also be applied to sol particles, of large refrative index but whose size parameter α does not exceed a certain value. The light scattering methods are more reliable than methods based on the transmission of light as the former is less likely to be affected by intrinsic absorption of light.

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